APPENDIX E

Shell Chemicals

The Development and Commercialization of Biodegradable Selectively Branched Detergent Alcohols

Louis Kravetz, David Singleton and Brendan Murray*
Shell Chemical LP
Westhollow Technology Center
Houston, TX 77082

Surfactants

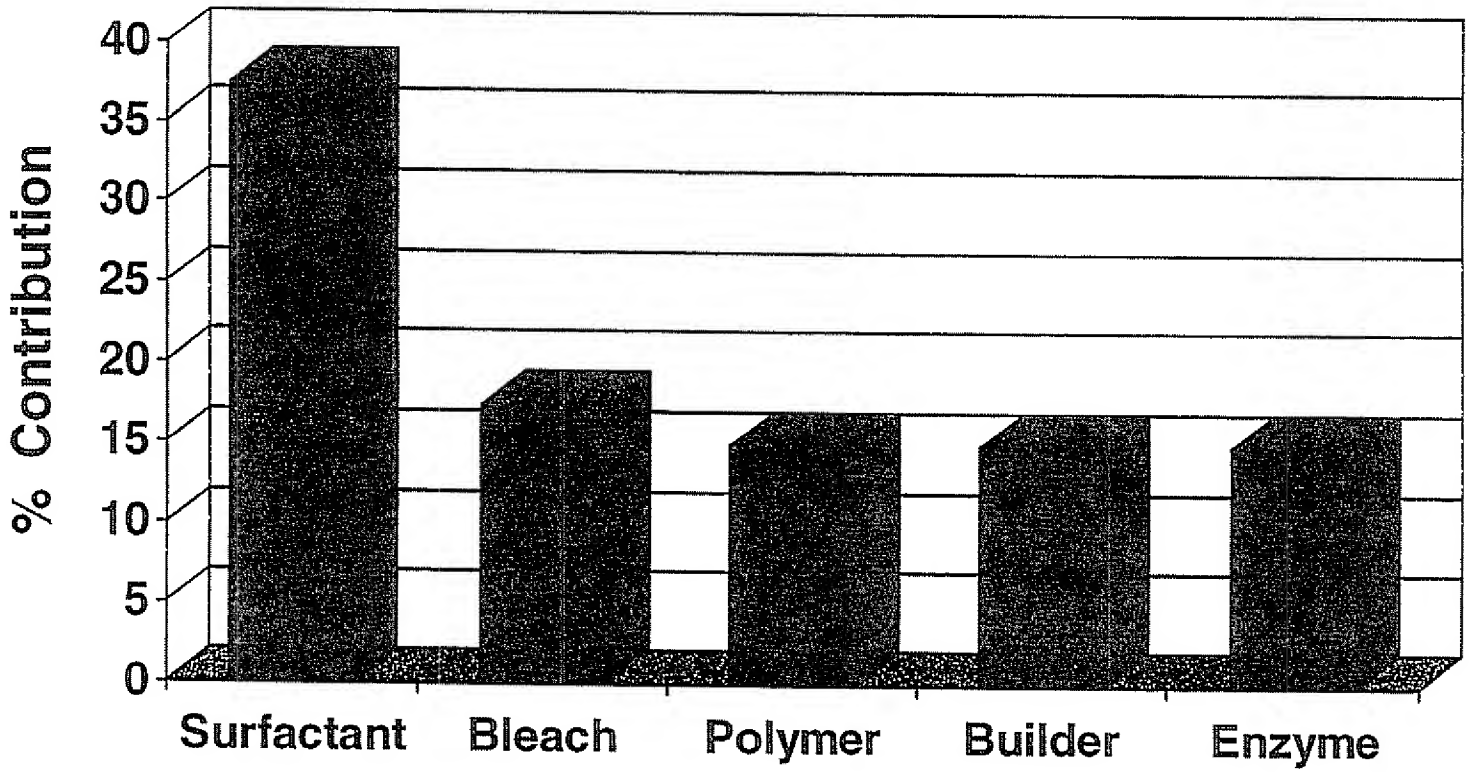
Multi-million ton/ year global business

Anionic surfactants are the largest group

They wet fabrics and soils; remove dirt and stains

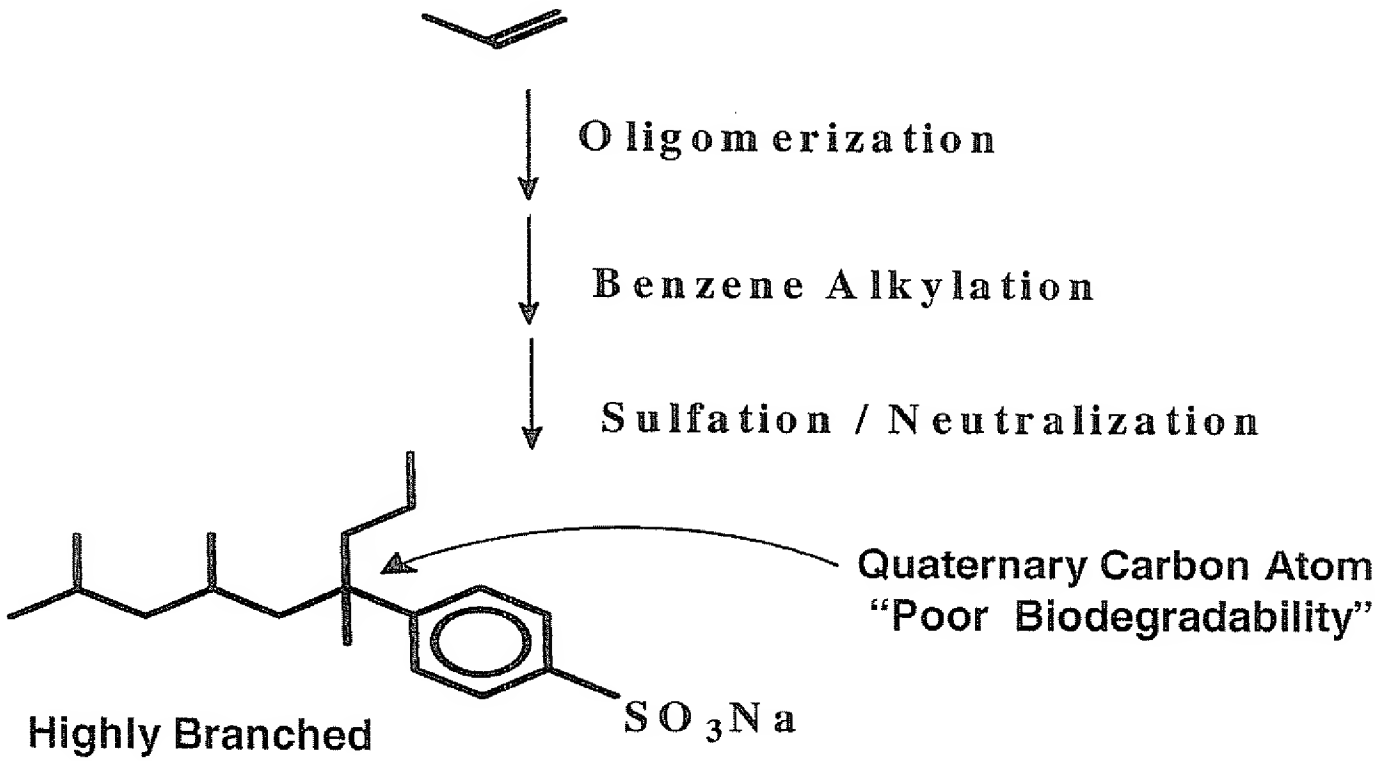
The single most important cleaning ingredient in most laundry and household cleaning products

Performance Contribution to Detergency



* G. Baillely et al., *Proceedings of the 5th World Conference on Detergents*, (2003)

1950's Vintage Alkylbenzene Sulfonate



Surfactant Events – A Need for Innovation

1950's - Highly Branched Alkylbenzene Sulfonates, (ABS)
slow biodegradation, foaming, aquatic toxicity?

1960's – ABS Regulation begins – Rapid replacement by
Biodegradable Linear Alkylbenzene Sulfonates,
Linear Alcohol Sulfates and Linear AES

A Paradigm is born: *"Alkyl branching is Bad"*

1970's - Movement to lower wash temperatures creates a
need for better cold water detergency

1980's *The Alkyl Branching Paradigm is Challenged*

2000's - High Solubility Biodegradable, Selectively
Branched Detergents are commercialized

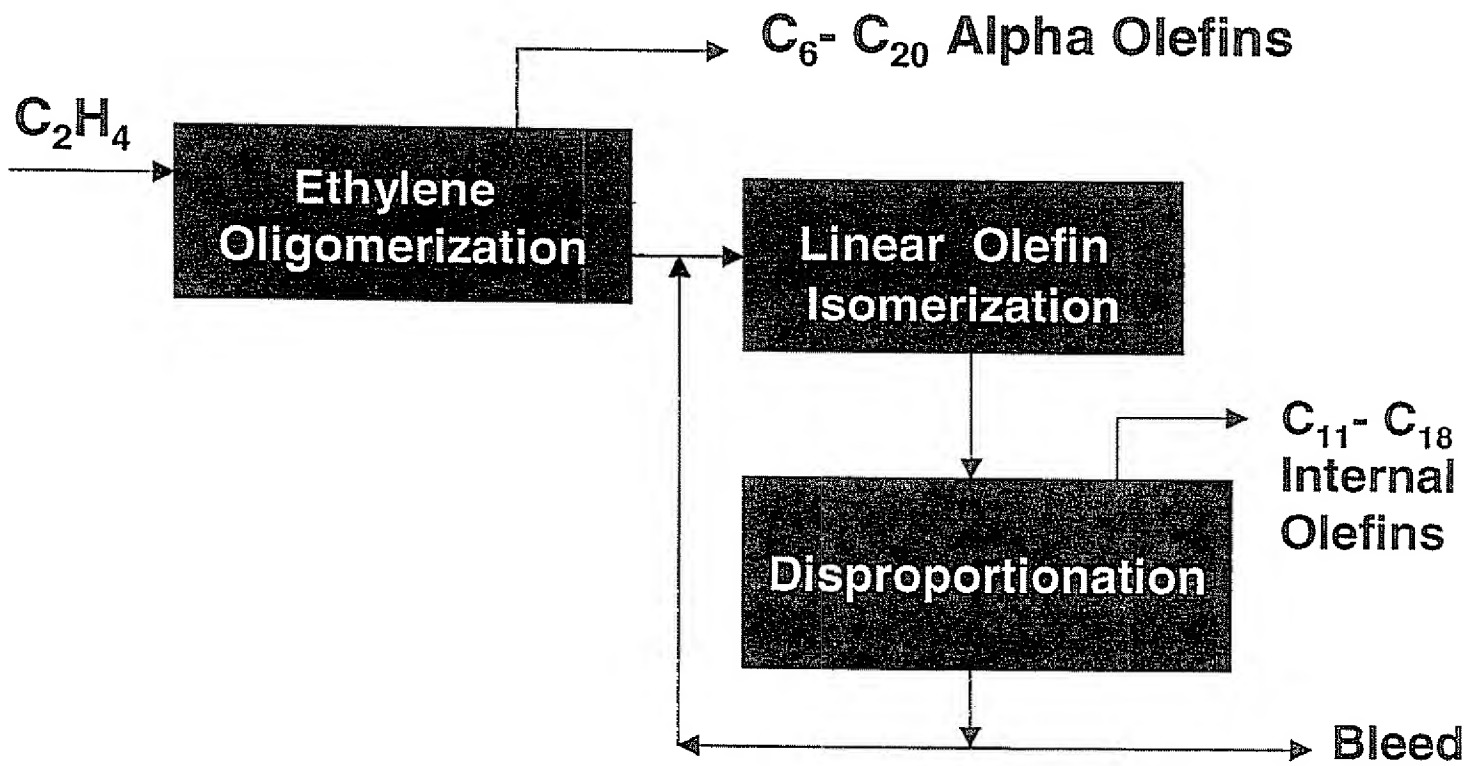
Recent Trends in Washing Processes

- Lower Wash Water Temperature
- Lower Energy Consumption
- Shorter Wash Times
- Reduced Water Usage

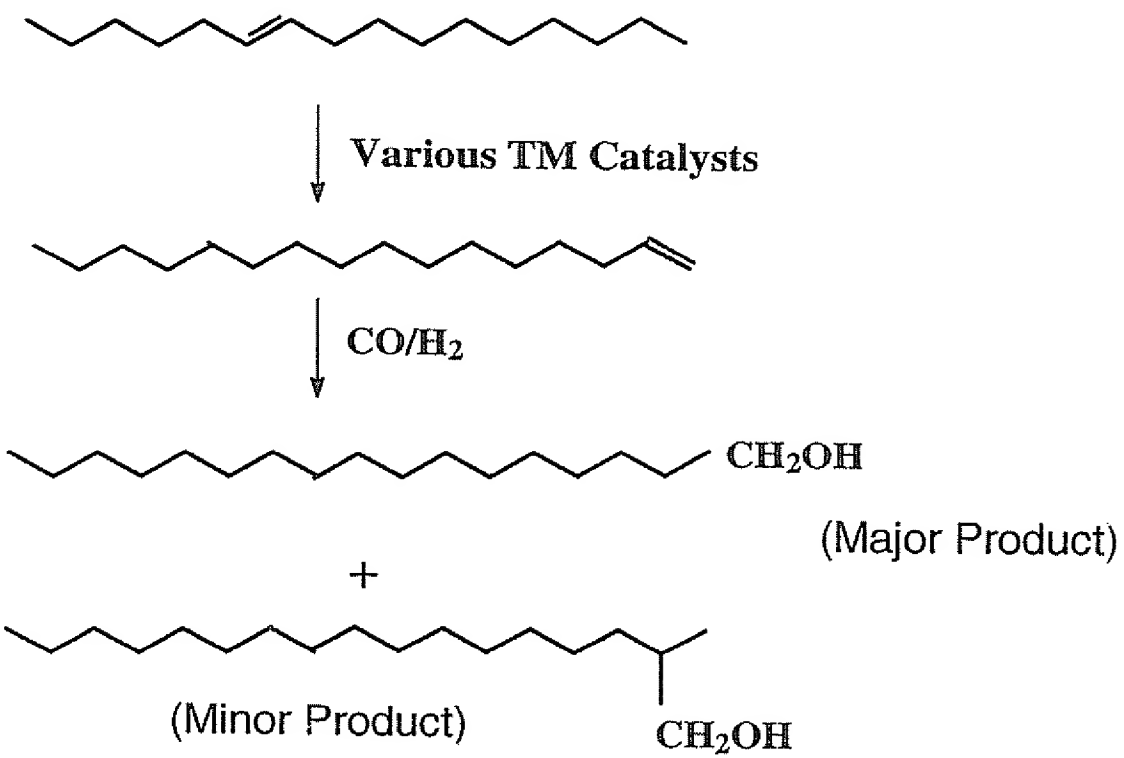
Desired Surfactant Properties

- Excellent Surface Activity
- Readily Biodegradable
- Superior Cold Water Detergency
- Improved Hard Water Solubility
- Ability to use Less Surfactant
- Affordable and Consistent Production

Shell Higher Olefins Process (SHOP)

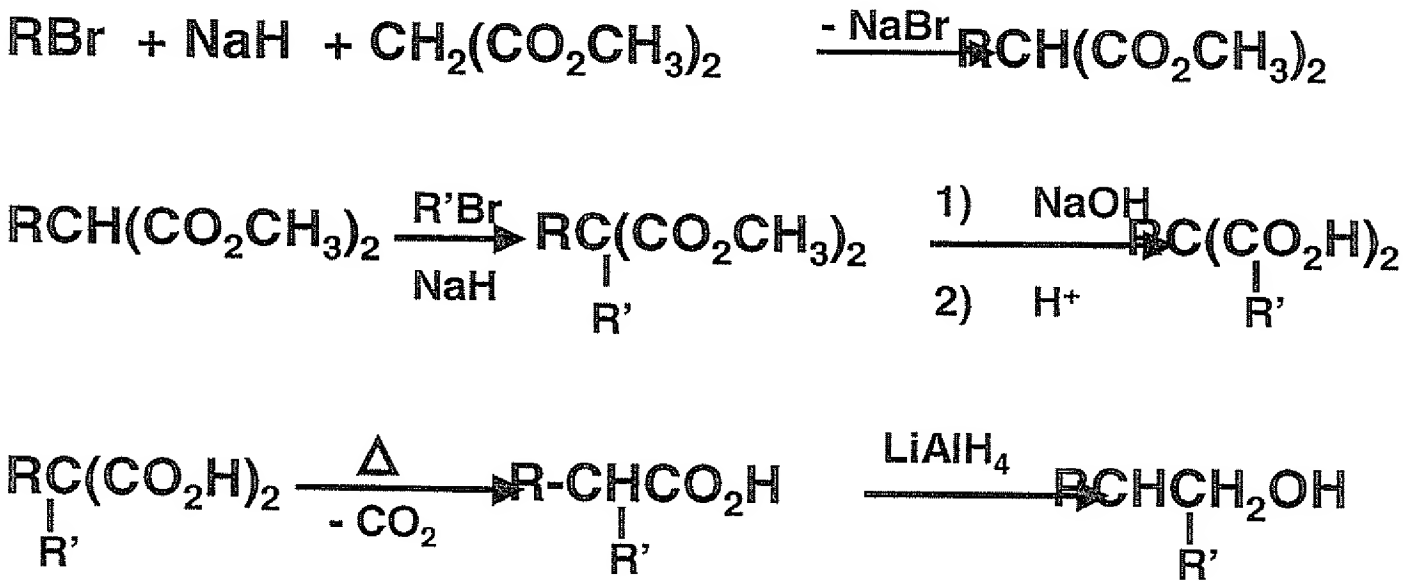


Shell Hydroformylation Process (SHF)



Model Compound Studies

Malonic Ester Synthesis of 2-Alkyl Branched Alcohols

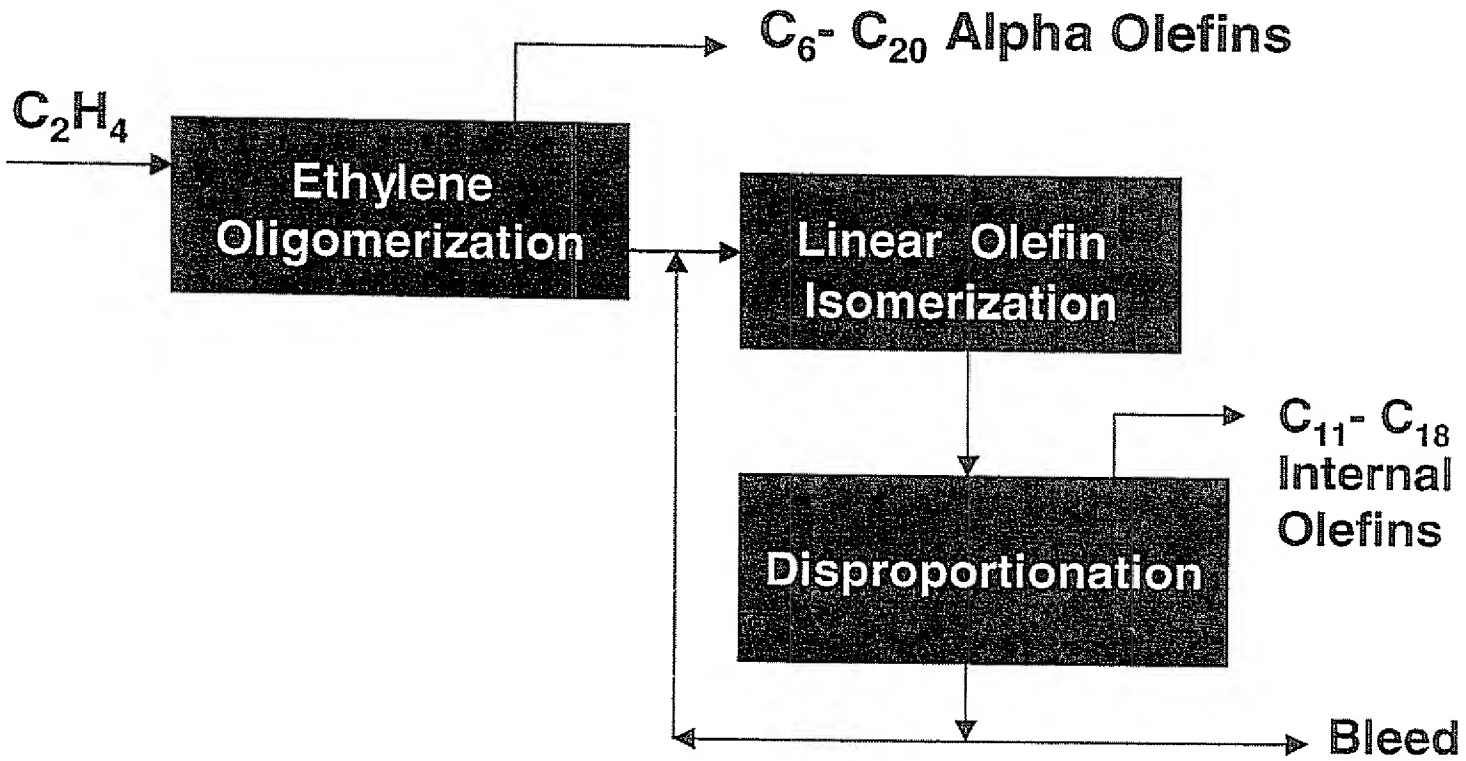


Alcohols were converted to the alcohol sulfate sodium salts by treatment with $ClSO_3H$, followed by neutralization with NaOH

How to Introduce Controlled Branching

- **Controlled Dimerization / Oligomerization of Lower Olefins**
- **Cross Metathesis Schemes**
- **Selective Skeletal Isomerization of Linear Olefins**
  - Use a proprietary, "pore engineered" zeolite catalyst
  - Makes mainly mono-branched olefins with the alkyl groups distributed at beneficial positions along the backbone
  - Very low level of quaternary carbon atoms in product

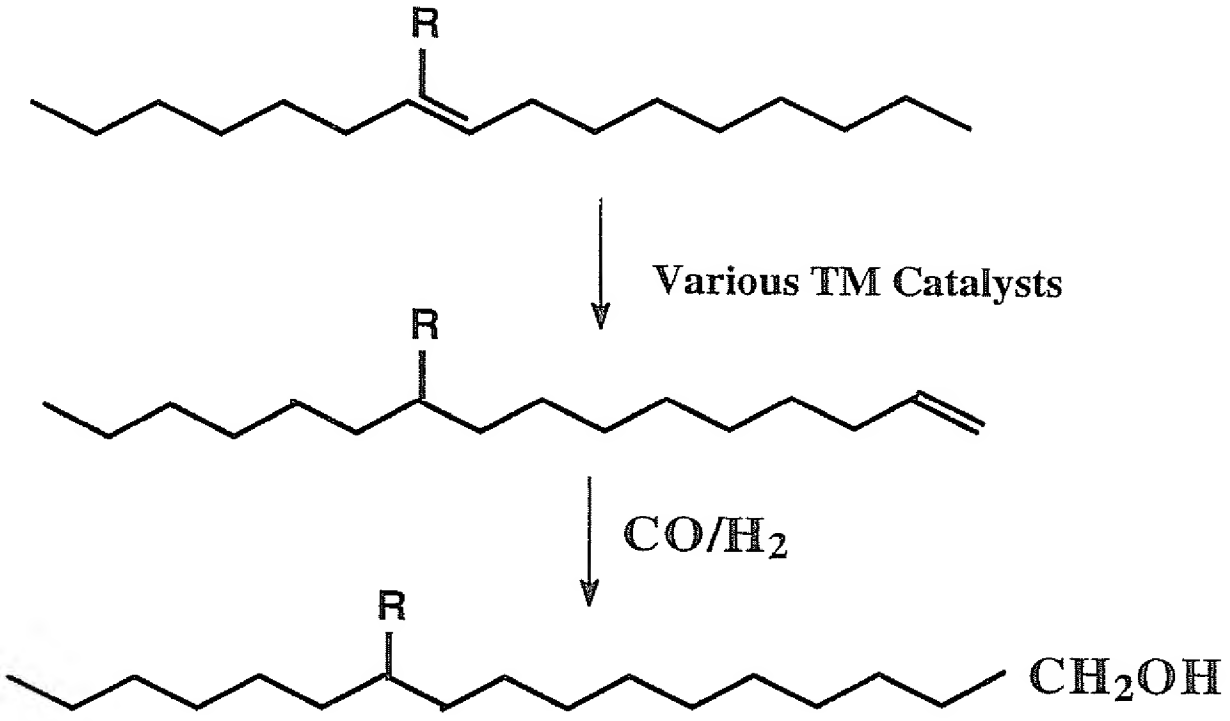
Shell Higher Olefins Process (SHOP)



Skeletal Olefin Isomerization Process

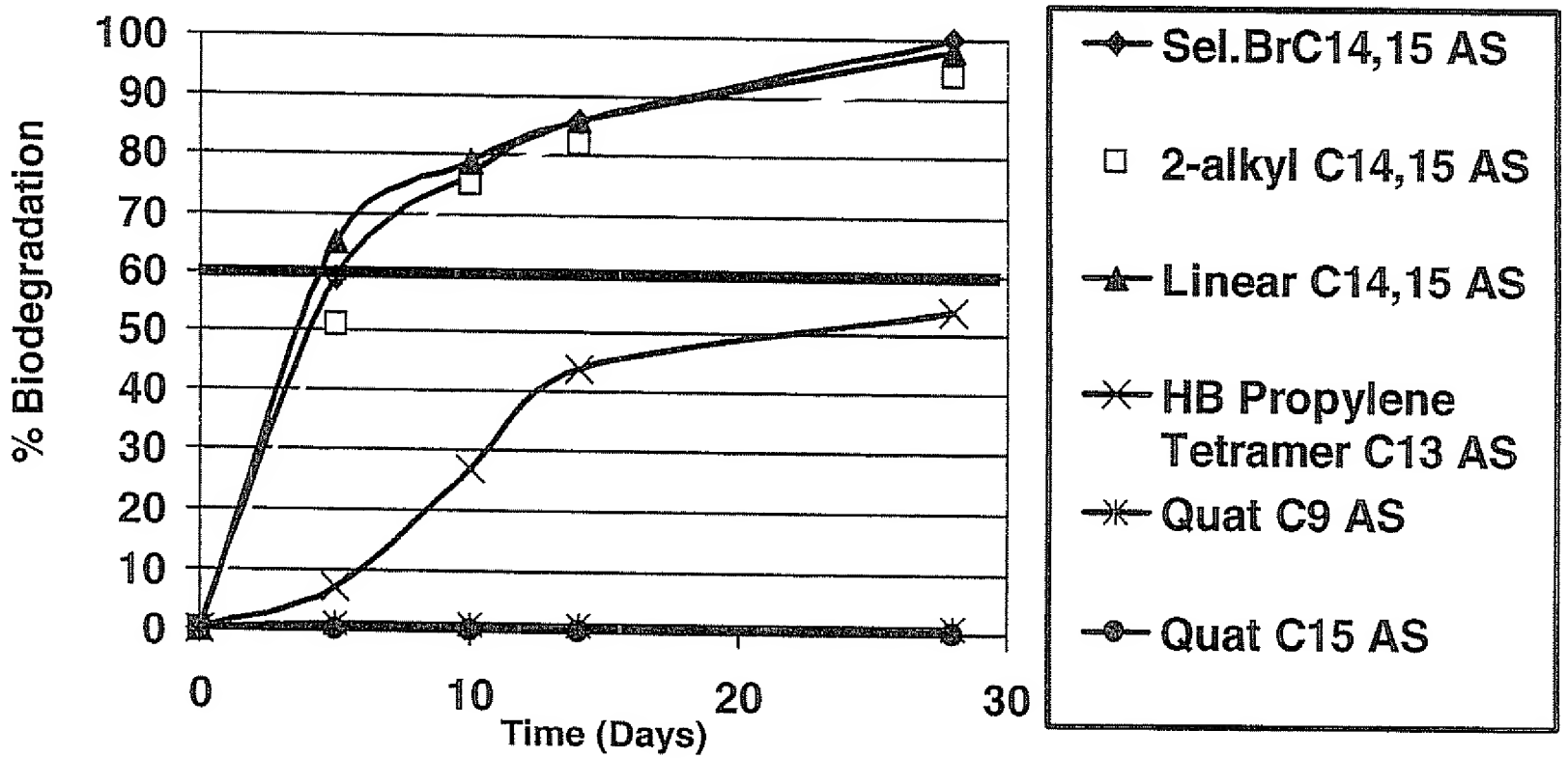
- Uses Alpha or Internal Olefins as Feedstocks
- Low Severity Operation
- Thermodynamic Equilibrium Conversion (>95%)
- Very High Selectivity (>98%)
- Multiply Regenerable Zeolite Catalyst
- Fully Compatible with the SHOP and SHF Processes
- Very High Catalyst Turnover Rate

Shell Hydroformylation Process

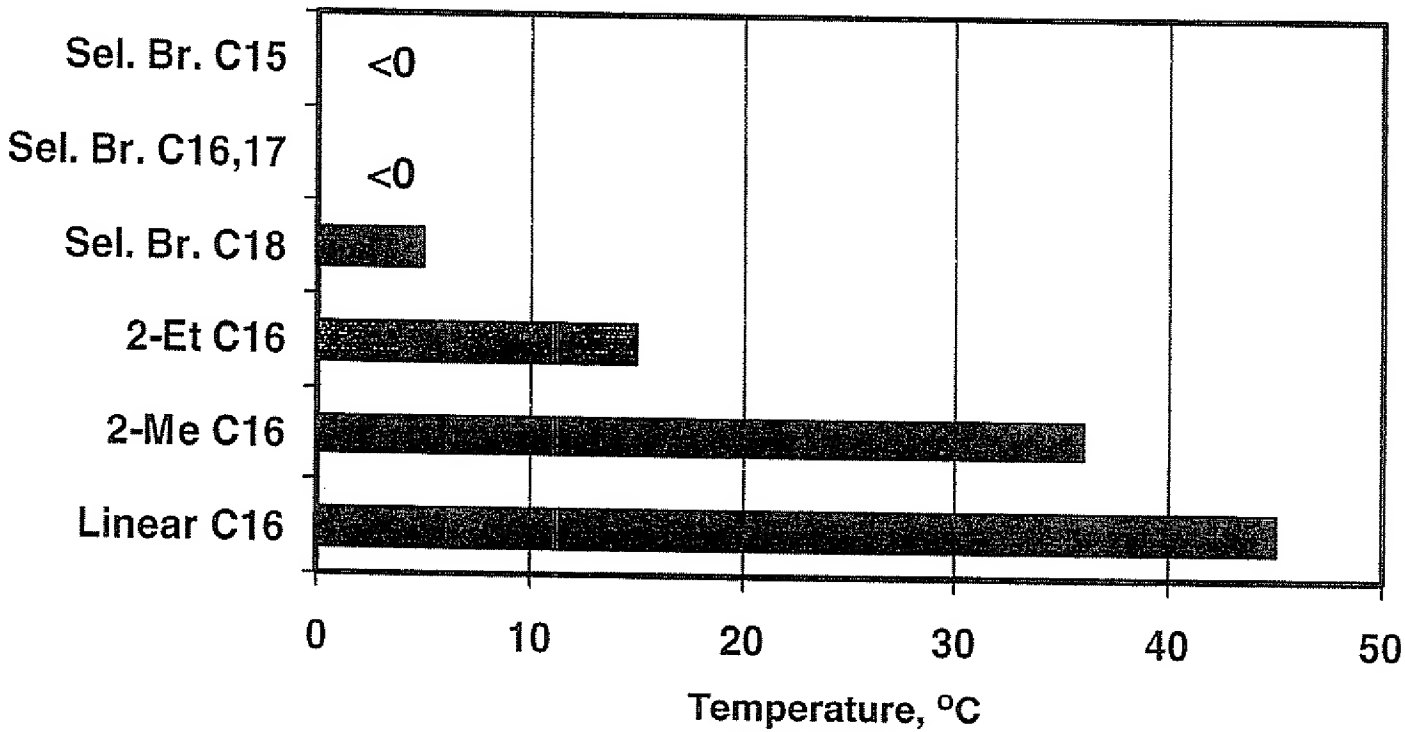


R distributed at desirable positions along backbone

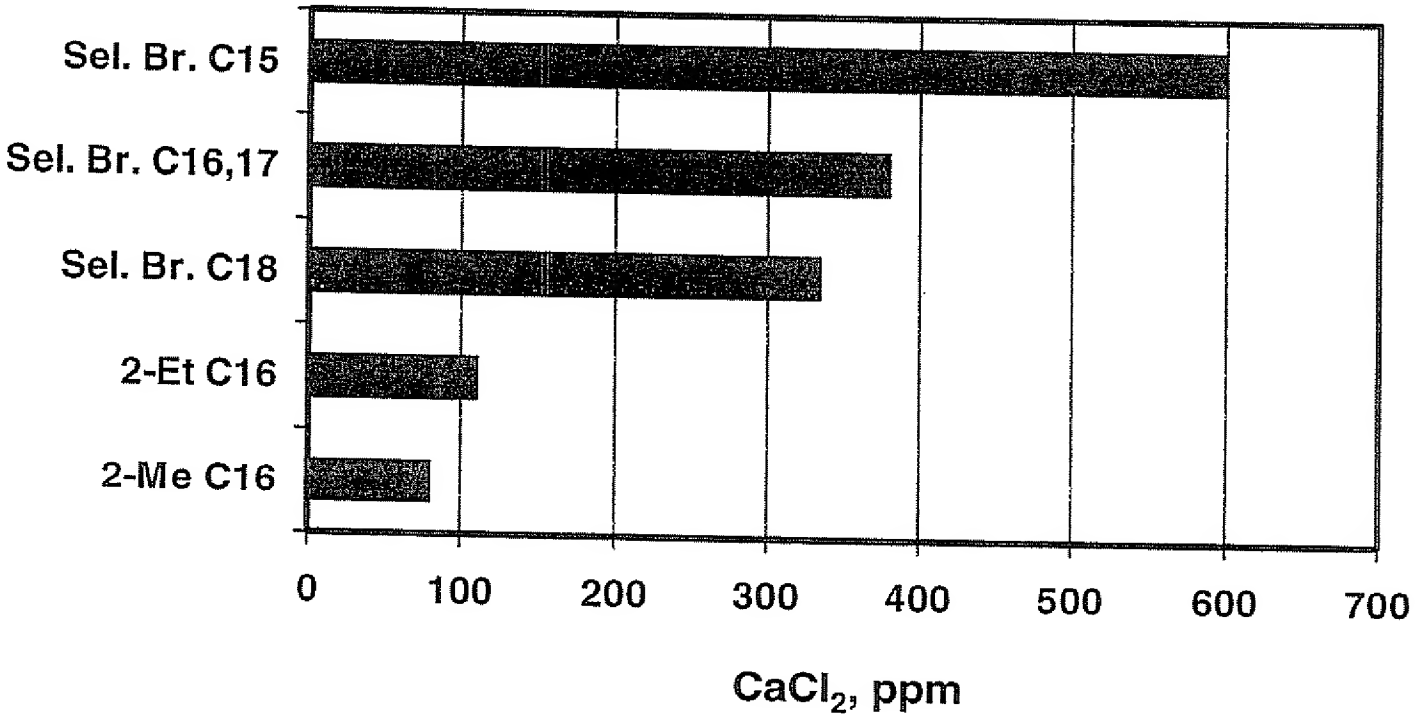
Closed Bottle Biodegradation Results for Various Alkyl Alcohol Sulfates



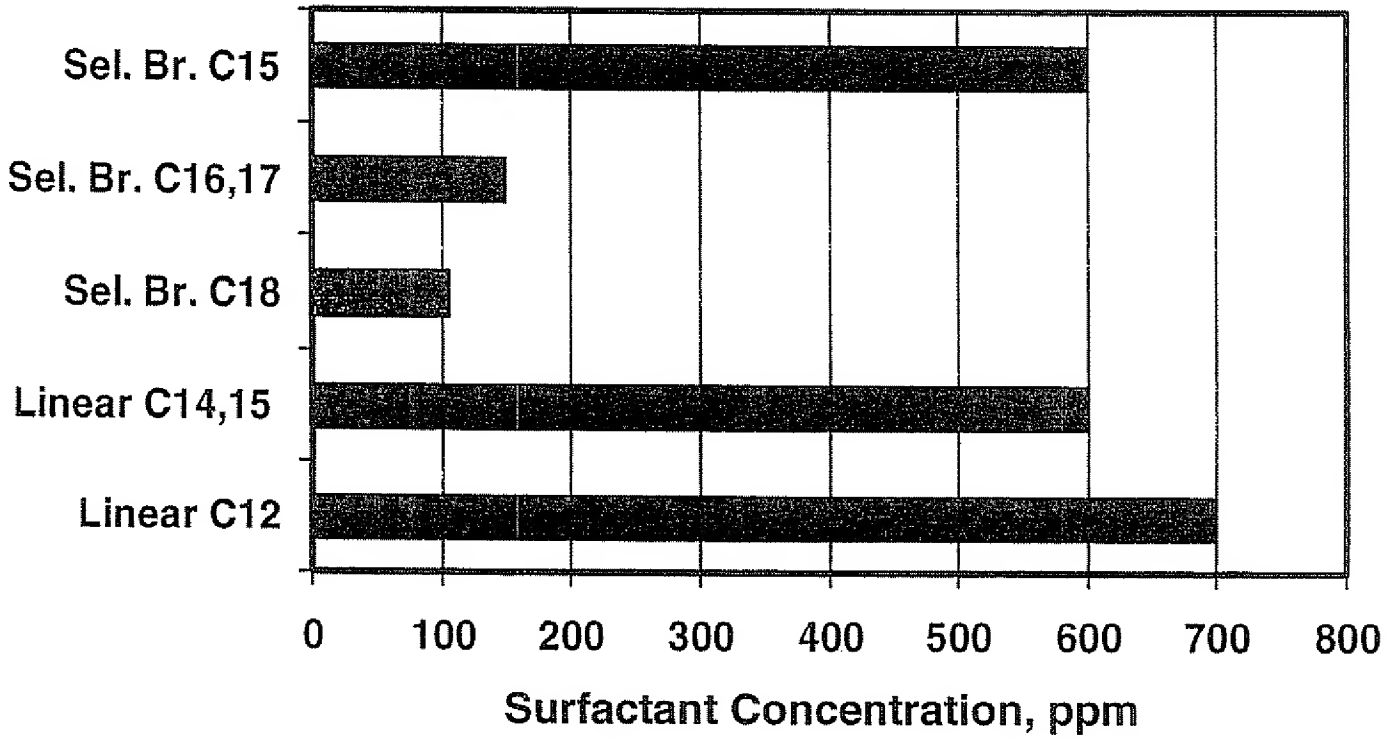
Krafft Temperature of the new Selectively Branched Alcohol Sulfates



Calcium Tolerance of the new Selectively Branched Alcohol Sulfates

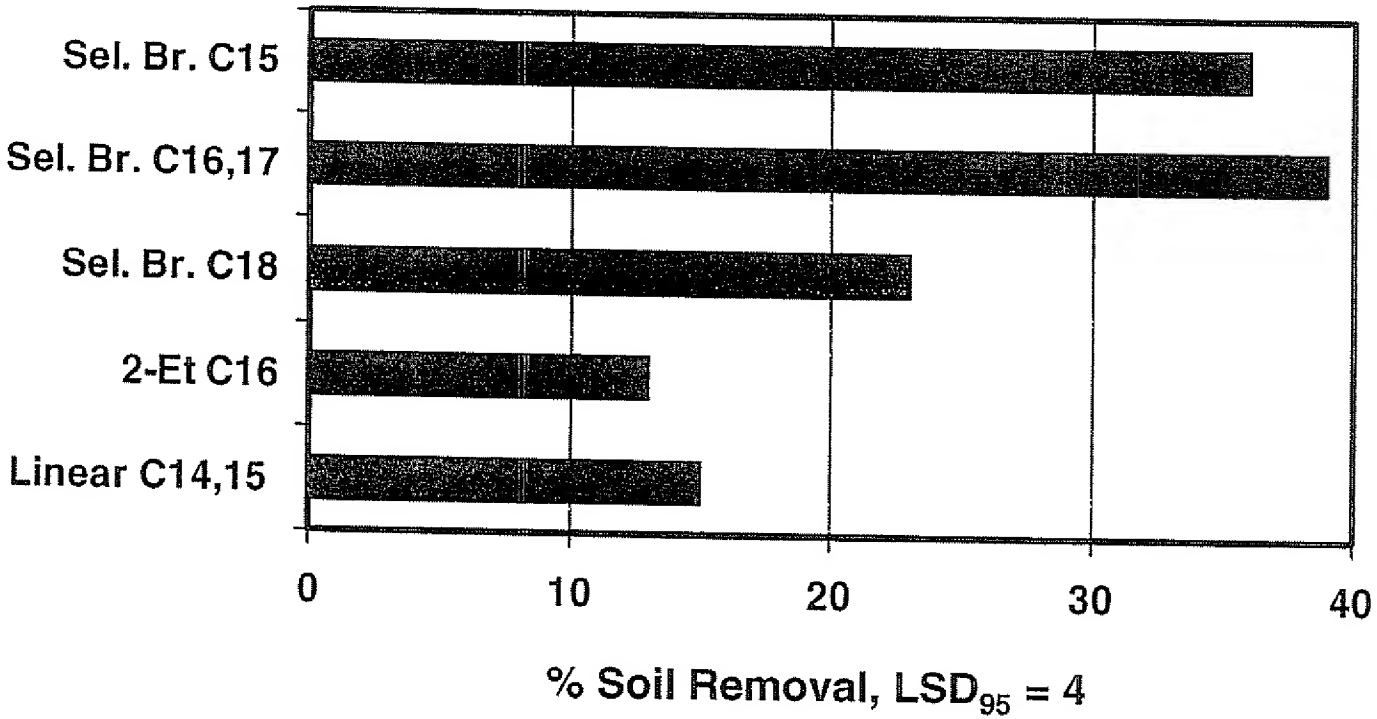


Critical Micelle Concentration of the Selectively Branched Alcohol Sulfates



Detergency Performance of the new Selectively Branched Alcohol Sulfates

(at 10°C and 150 ppm Water Hardness)



Partnering with Procter & Gamble

- P&G is a **Leading Global Supplier** to the Detergent Industry
- P&G conducted independent studies that pointed to a Primary Alcohol with a single methyl branch near the middle of the chain
- Evaluated various Shell "Selectively Branched" Alcohols
- Derivatized and formulated products based on the new alcohols
- A joint decision was made to commercialize the Innovation

Commercialization

- Product was scaled up in several stages (6, 50 and 3700 tonnes)
  - Allowed Process Modeling and Design Optimization
  - Customer feedback
- P&G worked closely with Shell during the Process
  - HS&E Studies, Alcohol Conversion and Product Formulation
  - Logistics, Product Specifications
  - Market Development Work
- World-Scale Olefin/Alcohol Plant built at Geismar, LA. in 2001
  - On spec product produced within 12 hours of feed-in
  - Breakthrough Technology Confirmed in Operations
- Alcohols successfully formulated into Quick Dissolving Tide®

"Tide is the most popular laundry detergent used in the USA"

New Opportunities

- **Personal Skin Care Products**
  - Excellent Emollient / Moisturizer
  - Non-oily
  - Good Viscosity and Solubility Characteristics
  - Biodegradable
- **Industrial Fluids**
  - Low Pour Point
  - Good Stability
- **Chemical Intermediates**
  - Novel Composition
  - Reagent for Various Industries

Acknowledgements

- The American Chemical Society
- Procter & Gamble
- Zeolyst International / CRI Catalyst Inc.
- Shell Chemical
  - GOAL Team - B. Colquhoun, B. Klein, P. Spicer, S. Sumrow
  - Geismar Plant and Engineering Staff
  - Scale-Up - B. Adkison, P. Ayoub, L. Gingrich, T. Hoewing, D. O'Neal
  - HODer - L. Fenouil, D. Haseltine, D. Johnson, S. Papitto, W. Schmidt, T. Thomason
  - Catalysis - B. Gambhir, D. Hamilton, B. Winquist
  - D. Holecek, VP Technology – Americas
  - F. Keeth, President - Shell Chemical LP